

===== WPI =====

TI - Finishing agent for paper - comprises graft starch polymer obtained by polymerising vinyl monomer mixture in aqueous solution containing cationic starch

AB - J10183493 A graft starch polymer is obtd. by polymerising a 20-80 pts.wt.- vinyl monomer mixt. in an aq. soln. contg. 20-80 pts.wt.-cationic starch.  
- The vinyl monomer mixt. comprises as its principal constituent:  
- (a) acrylamide and/or methacryl amide;  
- (b) anionic vinyl monomer copolymerisable with the amide; and/or  
- (c) a cationic vinyl monomer copolymerisable with the amide.  
- USE - Used for a finishing agent (claimed) used in recycling spoilage, or waste paper, and is used in size pressing, gate roll, and calendering in producing paper.  
- ADVANTAGE - The finishing agent exerts superior effects in paper surface strength, printability, ink jet printability, and paper maceration.  
- (Dwg. 0/0)

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PA - (SEIJ) SEIKO KAGAKU KOGYO KK

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===== PAJ =====

TI - SURFACE TREATING AGENT FOR PAPER

AB - PROBLEM TO BE SOLVED: To obtain a surface treating agent for paper manifesting an excellent effect on a surface strength and printing properties by including a grafted starch polymer obtained by polymerizing a specific vinyl monomer mixture in an aqueous solution containing a cationic starch as an active ingredient.  
- SOLUTION: A grafted starch polymer is obtained by polymerizing 20-80 pts.wt. vinyl monomer mixture comprising 50-99mol% acrylamide and/or methacrylamide, and 1-30mol% anionic vinyl monomer and 1-20mol% cationic vinyl monomer copolymerizable with the before vinyl monomer, in an aqueous solution containing 20-80 pts.wt. cationic starch, or by polymerizing 20-80 pts.wt. acrylamide and/or methacrylamide in an aqueous solution containing 20-80 pts.wt. cationic starch. The objective surface treating agent for paper is obtained by using the grafted starch polymer as an active ingredient.

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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention is excellent also in the disaggregation nature of paper, and offers the suitable coupling agent for recycling of a maculature or a waste paper while it demonstrates the effect excellent in the improvement in the surface intensity of paper, a printability, etc. about the coupling agent of paper about the coupling agent of the paper which turns into paper from a specific graft starch polymer in detail.

[0002]

[Description of the Prior Art] From the former, cellulose system polymer, such as starch, such as an oxidized starch, hydroxy ethyl ether-ized starch, and homemade denaturation starch, polyvinyl alcohol, acrylamide system polymer, and a carboxymethyl cellulose, a styrene-maleic-acid copolymer, a styrene-acrylic copolymer, a latex, vinyl acetate polymer, etc. are used as coupling agent of paper. In this, an oxidized starch, polyvinyl alcohol, acrylamide system polymer, etc. are used abundantly. However, in case starch and polyvinyl alcohol are used, a cooking process is required for them, the problem was in workability, and there was a problem of decomposition of foaming nature, dirt, and starch at the time of coating. Since acrylamide system polymer is equipped with the outstanding paper durability effect, although there is an inclination which the amount used increases, since it is expensive, the use has received economical restrictions. Moreover, the print sheet which carried out coating of the acrylamide system polymer tended to worsen the disaggregation nature of a maculature or a waste paper, and had the case where it became a problem from a viewpoint of recycling of paper.

[0003]

[Problem(s) to be Solved by the Invention] Improvement in the speed of the paper-making machine for the raw material of paper raising the rise of the rate of combination of recycled paper, closing-izing of the paper-making machine by drainage regulation, and productivity from an environmental problem in recent years and development of printing technology are remarkable, and upgrading, such as surface intensity of paper and a printability, is strongly demanded with improvement in the speed of a print speed, offset-izing, process-printing-izing, diversification of the printing method, and quality improvement. Especially in the printability, the improvement of the offset-printing aptitude corresponding to the dampening water in offset printing or the ink-jet printability corresponding to the water color ink in ink-jet record is called for strongly. Since it corresponds to these demands, a chemical is inner-\*\*<sup>(ed)</sup> to the pulp slurry of a paper-making process, or the outside \*\* method which carries out coating on the surface of paper is performed in it. Among these, if the yield is falling increasingly according to aggravation of paper-making conditions and inner \*\* carries out abundant addition of the chemical, the trouble of the dirt of a machine etc. will occur. On the other hand, it is known that the outside \*\* method which carries out coating on the surface of paper has a more advantageous yield from being about 100% and adhering to paper directly. However, although conventional coupling agent demonstrated the improvement effects, such as temporary surface intensity and a printability, it could not necessarily be called satisfying enough thing, but more highly efficient coupling agent was called

for. Furthermore, from a viewpoint of recycling of paper, coupling agent excellent in the disaggregation nature of a maculature or a waste paper was called for.

[0004]

[Means for Solving the Problem] As a result of repeating research wholeheartedly aiming at improvement of the coupling agent of paper, this invention person etc. found out having an effect with the polymer remarkable in upgrading, such as surface intensity of paper, and a printability, obtained by carrying out the graft polymerization of the specific vinyl monomer in the solution containing cation nature starch, and excelling in the disaggregation nature of a maculature or a waste paper, and completed the coupling agent of this invention.

[0005] It is under [ solution / in which this invention contains cation nature starch 20 - 80 weight sections ] setting. Namely, the (a) acrylamide and/or a meta-acrylamide (it considers as a "(meta ) acrylamide" below), (b) The polymerization of the vinyl monomer mixture 20 which makes a principal component at least one sort chosen from the cation nature vinyl monomer which may be copolymerized for the anionic vinyl monomer and (c) aforementioned a component which may be copolymerized for the aforementioned a component - the 80 weight sections is carried out. It is the surface-size agent of the paper which makes an active principle the graft starch polymer obtained.

[0006] Moreover, this invention is the coupling agent of the paper which makes an active principle the graft starch polymer obtained in the solution containing cation starch 20 - 80 weight sections by carrying out the polymerization of an acrylamide (meta) 20 - the 80 weight sections.

[0007]

[Embodiments of the Invention] Hereafter, this invention is explained more to a detail. With the cation nature starch used for this invention, a cation nature machine is introduced into starch and/or denaturation starch according to a conventional method. The etherification which is the various starch used as raw materials, such as corn, wheat, a potato, tapioca, and rice, and a denaturation object of those as an example, esterification, oxidization, enzyme denaturation starch, etc. can be mentioned, and these one sort or two sorts or more are used.

[0008] In addition, the viscosity of the cation starch used for this invention has the desirable range of 50-1000cps (30 degrees C) at 30% of concentration.

[0009] Manufacture of cation nature starch makes at least one sort of basic nitrogen chosen from the group which becomes starch and/or denaturation starch from each amino group of the first class, the second class, and the third class, and the fourth class ammonium contain. As for the content of basic nitrogen, it is desirable that it is 0.1 % of the weight or more. What is necessary is just to make the cation-ized agent which becomes starch and/or denaturation starch by the reactant of a dialkyl amine or alkylamine, and EPIKUROHI drine compounds specifically react.

[0010] The thing of the hypoviscosity prepared by decomposing the cation starch which cation-ized the thing, starch, and/or denaturation starch which cation-ized conventionally the denaturation starch which decomposed the various aforementioned starch with enzymes, such as an amylase, especially by the well-known method using the cation-ized agent with enzymes, such as an amylase, is desirable.

[0011] In this invention, the either may be independently used for an acrylamide (meta), and it may use both together.

[0012] As an anionic vinyl monomer used for this invention, those sodium, such as an acrylic acid, a methacrylic acid, an itaconic acid, a maleic anhydride, a fumaric acid, a vinyl sulfonic acid, a styrene sulfonic acid, and a 2-acrylamide-isobutane sulfonic acid, or a potassium, an ammonium salt, etc. may be mentioned, these one sort may be used independently, and two or more sorts may be used together.

[0013] As a cation nature vinyl monomer used for this invention N. N-dimethylaminoethyl (meta) acrylate, N.N-diethylaminoethyl (meta) acrylate, N. N-dimethylamino propyl (meta) acrylate, an N.N-dimethylaminoethyl (meta) acrylamide, N. N-dimethylamino propyl (meta) acrylamide, a vinylpyridine, The vinyl monomer which has the 3rd class amino groups, such as a vinyl imidazole, an arylamine, and a diarylamine Or those hydrochlorides, a sulfate, formate, acetate, and a sulfamate are mentioned. Furthermore, the alkyl halide containing the 3rd class amino group, such as a vinyl monomer and methyl chloride, Arylated-alkyl halide, such as a benzyl star's picture, a dimethyl sulfate, A diethyl sulfate.

EPIKUROHI drine compounds, 3-chloro-2-hydroxypropyl trimethylammoniumchloride, The quarternary ammonium salt obtained by the reaction with the 4th class-ized agents, such as glycidyl alkylammonium chloride, is also usable, these one sort may be used independently, and two or more sorts may be used together.

[0014] In addition, the (a) (meta) acrylamide, (b) anionic vinyl monomer and (c) cation nature vinyl monomer, and the vinyl monomer that can be copolymerized can be made to contain in this invention in the range which does not exceed ten-mol %. A diisopropyl acrylamide besides various cross-linking vinyl monomers, such as a MECHIRORU (meta) acrylamide, a dimethyl acrylamide, two functionality, three functionality, and four functionality, styrene allyl alcohol, acrylic (meta) ester, acrylonitrile, vinyl acetate, hydroxyl content (meta) acrylic esters, a vinyl pyrrolidone, etc. can be used for this kind of monomer.

[0015] Manufacture of the graft starch polymer in this invention can be conventionally performed by various well-known methods. For example, the solution of cation nature starch described above in the reaction container equipped with stirring and the nitrogen gas introduction pipe and said monomer component (a). At least one sort and water which were chosen from said monomer component (b) and said monomer component (c) are prepared. As a polymerization initiator, a hydrogen peroxide, an ammonium persulfate, potassium persulfate, The redox initiator which combined peroxides, such as ammonium hydroperoxide, or these peroxides, and reducing agents, such as a bisulfite Or water-soluble azo system polymerization initiators, such as a 2-2' azobis (2-AMINOJI propane) hydrochloride, etc. are used, and if it is made to react with the reaction temperature of 40-80 degrees C for 1 to 5 hours, the graft starch polymer made into the purpose can be obtained.

[0016] In addition, it faces manufacturing the graft starch polymer in this invention. the monomer mixture which consists of (a) (meta) acrylamide 50 - 99-mol %, (b) anionic vinyl monomer 1 - 30-mol %, and (c) cation nature vinyl monomer 1 - 20-mol % into the solution containing cation nature starch 20 - 80 weight sections -- or (a) (meta) It is desirable to carry out the polymerization of the monomer mixture which consists of acrylamide 80 - 99-mol % and (b) anionic vinyl monomer 1 - 20-mol %, or (meta) the monomer component chosen from acrylamide 100 mol %. In addition, when cation nature starch is under 20 weight sections, a problem is in the disaggregation nature of paper, and if 80 weight sections are exceeded, the surface intensity of paper and a printability will become bad.

[0017] The graft starch polymer in this invention is usually obtained in the form of water distribution liquid of about about 10 - 40 % of the weight of solid-content concentration.

[0018] Although the coating concentration of the coupling agent of the paper concerning this invention is determined by the quality which the liquid adsorption (coating weight) of application stencil paper and paper require, 0.5 - 10 % of the weight of solid contents and the amount of coating are usually a solid content 0.05 - 2 g/m<sup>2</sup>.

[0019] Coating of the coupling agent of the paper concerning this invention can be carried out by size press, a gate roll, a blade coating machine, the calender, the bar coating machine, the knife coating machine, the air knife coater, etc. In addition, a spray method, the sinking-in method, etc. are adopted arbitrarily.

[0020] Especially the stencil paper that carries out coating of the coupling agent concerning this invention is not limited, and is not restricted to pulp, a loading material, an inner \*\* sizing compound, a paper reinforcing agent, a yield agent, etc.

[0021] It can be used for acid paper making from all neutral paper making, for example, can be used for a paper-of-fine-quality, report-grade-paper, coat paper, newsprint, converting-paper, liner, white-paperboard, PPC form, ink-jet form, thermal paper, special paper, and toner printer form, plaster-board stencil paper, etc.

[0022] In addition, to the coupling agent of the paper of this invention, a surface-size agent, antiseptics, a defoaming agent, a viscosity controlling agent, a color, starch, polyvinyl alcohol, etc. can be added.

[0023]

[Example] Hereafter, although this invention is explained more to a detail based on an example and the example of comparison, this invention is not limited to these examples.

[0024] Example 1: After having mixed the cation nature tapioca starch (30 % of the weight solution [ of concentration ], viscosity [ of 25 degrees C / of 350cps ], (degree DS) of substitution 0.05, 0.4 % of the weight of nitrogen contents) 166.7 section, the acrylamide 44.94 section, and the acrylic-acid 5.06 section, adding water and making the whole quantity into the 450 sections, 10% of the weight of caustic potash was added, and it adjusted to pH 5.0. The whole quantity was put in into the flask which attached the agitator, after performing an ammonium persulfate and the 0.08 sections each of a sodium bisulfite at warming and 55 degree C of inside \*\* and performing polymerization reaction at addition and 65-70 degrees C in a water bath for 3 hours, cooling and water were added and 20.5% solution of solid-content concentration of the graft starch polymer of this invention which has the viscosity of 9500cps of 25 degrees C was obtained by making the whole quantity into the 500 sections.

[0025] Examples 2-10: In the example 1, changed the kind of cation nature starch, the weight rate of a vinyl monomer and the kind of vinyl monomer component, and its combination composition (mol %) as in Table 1, and the amount of an ammonium persulfate and the sodium bisulfite used was changed suitably, and also the graft starch polymer was obtained by the same method as an example 1. The character is written together to Table 1.

[0026]

[Table 1]

表1

表面処理剤	カチオン澱粉		CS/17-	モノマー成分				pH	固形分	粘度
	種類	粘度25°C		重量比	(a) 成分	(b) 成分	(c) 成分			
実施例 1	タapioca DS 0.05	350 cps 30%	1 / 1	AAM 95mol%	AA 5mol%	—	—	5.50	20.5	9200
2	〃	〃	1 / 1	AAM 91mol%	AA 3mol%	DMAPAA 6mol%	—	5.62	20.7	12100
3	〃	〃	2 / 1	AAM 94.99mol%	IA 5mol%	—	MBAA 0.01mol%	5.48	20.8	11300
4	〃	〃	1 / 2	AAM 91.99mol%	AA 3mol%	DM 5mol%	MBAA 0.01mol%	5.66	20.6	5800
5	カ-2 DS 0.1	290 cps 30%	1 / 2	AAM 95mol%	AA 5mol%	—	—	5.35	20.5	10500
6	馬鈴薯DS 0.15	395 cps 30%	1 / 1	AAM 98mol%	AA 2mol%	—	—	5.44	20.4	10800
7	タapioca DS 0.05	200 cps 30%	1 / 1	AAM 82mol%	AA 3mol%	DMAPAA 15mol%	—	5.27	20.1	13400
8	〃	〃	1 / 1	AAM 85mol%	AA 15mol%	—	—	5.13	20.7	11200
9	〃	〃	1 / 2	AAM 100mol%	—	—	—	5.31	20.3	7300
10	〃	〃	2 / 1	AAM 100mol%	—	—	—	5.24	20.0	8500

・CS : カチオン性澱粉  
 ・AAM : アクリルアミド  
 ・AA : アクリル酸  
 ・IA : イタコン酸

・DM : N,N-ジメチルアミノエチルメタクリレート  
 ・DMAPAA : N,N-ジメチルアミノプロピルアクリルアミド  
 ・MBAA : メチレンビスアクリルアミド

[0027] [Performance evaluation of coupling agent] The performance evaluation was performed about the well-known coupling agent shown in the coupling agent and the examples 1-3 of comparison of paper concerning this invention shown in the aforementioned examples 1-10.

[0028] (1) Stencil paper for coating : the acid paper-making paper of fine quality which has the quality of paper for Stockigt-sizing-degree 3 seconds by rice basis-weight 65 g/m<sup>2</sup> and the JIS method was used as stencil paper for coating.

[0029] (2) Surface coating method : the coating liquid which diluted each coupling agent with water so that coating weight might become 0.5 g/m<sup>2</sup> by the solid content was used for the stencil paper for coating, double-sided coating of the roll coater was carried out, with the rotation dryer, it dried for 1

minute and 110 degrees C of surface coating were performed. the coverage of the coupling agent of the test paper, and quality of paper -- evaluation is as being shown in Table 2  
[0030] (3) the quality of paper of coupling agent -- appraisal method;

(a) IGT test : print with an IGT printing testing machine and express as the acceleration which starts picking.

used testing-machine: -- IGT printability-tester use ink [ by Kumagai \*\*\*\* Industrial company ]: -- the Toyo Ink make and 15 articles of Japanese ink ink TV affair: -- printing pressure 50 kg/m<sup>2</sup> and tension

(b) RI test : RI printing testing machine (made in the Ming factory) performs a printing test, and evaluate the state of picking in five stages of 5 A - \*\* 1.

(c) water resistance [ of ink-jet printed matter ]: -- bleeding according [ after using an ink jet printer and performing ink-jet printing, drop waterdrop on a printing side, suck up by the after / 1 minute / blotting paper, and ] to the water of printed matter -- a judgment (x \*\* O excellent -- it is usually inferior)

(d) Wax pick (A) : measure the surface intensity by Dennison wax No.

(e) Disaggregation nature test : 1g of pieces of paper which cut the surface coated paper into 5mm angle was put in into 100g of 30-degree C water, and stirring disaggregation was carried out for 5 minutes with the high-speed agitator (2000rpm). Paper making of the slurry after disaggregation is carried out with an extract testing machine, and a disaggregation state is evaluated in five stages of 5 A - \*\* 1.

[0031]

[Table 2]

表2

表面処理剤		塗布量 g/m <sup>2</sup>	IGT テスト cm/s	RI テスト	インクフュット 耐水性	ワックスピック A	離解性 テスト
実施例 1		0. 48	233	4	○~△	13~14	3~4
2		0. 51	248	4~5	○	14	4
3		0. 53	220	4	○~△	13	4~5
4		0. 54	255	5	○	14	4
5		0. 49	263	5	○~△	14	3~4
6		0. 50	236	4	○~△	14	4
7		0. 57	237	4	○	13~14	3~4
8		0. 49	225	4~5	○~△	14	4~5
9		0. 55	260	5	○~△	14	3~4
10		0. 60	219	4	○~△	13	4~5
比較例 1	酸化澱粉	0. 59	72	3	×	10	4~5
2	PVA	0. 45	215	4	△	14	2~3
3	A-PAM	0. 55	228	4	○~△	14	1
ブランク	—	—	48	1	×	7	5

酸化澱粉 [日本食品加工(株)製、商品名MS-3800]

PVA (ポリビニルアルコール) [クラレ(株)、商品名PVA-117]

A-PAM (アニオニ性ポリアクリルアミド) [星光化学工業(株)製、商品名XコートP-130:濃度20%品]

[0032]

[Effect of the Invention] The coupling agent of the paper concerning this invention is used by the size press of a paper manufacture process, the gate roll, calender coating, etc., demonstrates the effect excellent in the improvement in the surface intensity of paper, a printability, an ink-jet printability, etc., and since it excels in the disaggregation nature of paper, it is suitable for recycling of a maculature or a waste paper.

[0033] Therefore, it can be said that the industrial availability of this invention is very large.

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[Translation done.]